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1. AGENCY USE ONLY (Leave blank) 31 March 2000 FINAL - 1 March 1996-31 October 1999 4. TITLE AND SUBTITLE 5. FUNDING NUMBERS Studies of Latent Acidity and Neutral Buffered C/F49620-96-1-0097 Chloroaluminate Ionic Liquids 6. AUTHOR(S) Robert A. Osteryoung 7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) 8. PERFORMING ORGANIZATION REPORT NUMBER North Carolina StateUniversity Box 7003 Raleigh, NC 27695-7003 9. SPONSORING / MONITORING AGENCY NAME(S) AND ADDRESS(ES) 10. SPONSORING / MONITORING **AGENCY REPORT NUMBER** AFOSR/NL 801 North Randolph St., **Room 732** Arlington, VA 22203-1977 11. SUPPLEMENTARY NOTES 12a. DISTRIBUTION / AVAILABILITY STATEMENT 12b. DISTRIBUTION CODE APPROVED FOR PUBLIC RELEASE; DISTRIBUTION UNLIMITED 13. ABSTRACT (Maximum 200 Words) Studies on ionic liquids/composed of aluminum chloride and 1-ethyl-3-methylimidazolium chloride were carried out, with emphasis on understanding and explaining acidity and latent acidity in "neutral buffered" melts. It was found that alkaline earth, as well as alkali metal salts, function as buffering agents, with both showing the "latent acidity" effect. Both Brønsted and Lewis acidities were investigated in an effort to understand the role of the type and concentration of the "buffering" alkali or alkaline earth salt. A silver/silver chloride/chloride ion electrode was found to function as a reversible chloride ion indicator over a very narrow range of melt acidity about the neutral point. This electrode, and relative solubility product measurements, were employed in these studies. It was found that the latent acidity could be explained in terms of the solubility product relationship of the buffering salt, with the salt having the smallest solubility product creating the most acidic melt. Some work was also carried out on non-

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haloaluminate melts.

SUMMARY OF WORK, 1 March, 1996 – 31 October, 1999

Completed Work

I. Work Carried Out Under Previous Grant

Several manuscripts listed as "in press" or as "submitted" in the Final Report on Contract F49620-94-J-0056, "Chemical Studies in Lewis Acid and Suuperacid Systems", have been published. These include:

J. Fuller, R. T. Carlin, and R. A. Osteryoung, "In-Situ Optical Microscopy Investigations of Lithium and Sodium Film Formation in Buffered Room Temperature Molten Salts", J. Electrochem. Soc., **143**, L45 (1996).

Richard T. Carlin, Paul C. Trulove, Robert A. Mantz, John J. O'Dea and Robert A. Osteryoung, "Electron Transfer Kinetics for Weakly-Bonded Labile Metal-Ligand Complexes", Royal Society of Chemistry, Faraday Transactions, Special Issue on Electrochemistry Honoring Roger Parsons, **92**, 3969-3973 (1996)

Robert A. Mantz, Paul C. Trulove, Richard T. Carlin, and Robert A. Osteryoung, "Gutmann Acceptor Properties of LiCl, NaCl, and KCl Buffered Ambient-Temperature Chloroaluminate Ionic Liquids", Proceedings of Tenth International Symposium on Molten Salts, R. T. Carlin, S. Deki, M. Matsunaga, D.S. Newman, J. R. Selman and G. R. Stafford, Eds., Proceedings Volume 96-7, pgs. 104-115, The Electrochemical Society, Pennington, NJ (1996).

Dawn King and Robert A. Osteryoung "Acidity of HCI in Neutral Buffered Chloroaluminate Molten Salts", Proceedings of Tenth International Symposium on Molten Salts, R. T. Carlin, S. Deki, M. Matsunaga, D.S. Newman, J. R. Selman and G. R. Stafford, Eds., Proceedings Volume 96-7, pgs. 80-91, The Electrochemical Society, Pennington, NJ (1996)

This prior but now published work was described in the previous Final Report on Contract F49620-94-J-0056.

Most of the work carried out under this present contract has been published, is in press, or has been submitted for publication. Titles and Abstracts of the work follow.

II. Work Completed Under Present Grant

A. Acidity and Latent Acidity in Haloaluminate Ionic Liquids

Acidity of HCl in Neutral Buffered Chloroaluminate Molten Salts, Dawn King, Robert Mantz, and Robert A. Osteryoung, J. Am. Chem. Soc., 118, 11933-11938 (1996). — (Appendix A- Ref. 141).

Abstract: The Brønsted acidity of HCl in neutral buffered AlCl₃-2-ethyl-3-methylimidazolium chloride (EMIC) melts has been compared to the Brønsted acidity of HCl in acidic (55 mol % AlCl₃) melts. The acidities were compared using the spectrophotometric indicated method. Arenes were used as the weak indicator bases. The acidity of HCl in the neutral buffered melts was found to be dependent on both the type of buffering agen (LiCl, KCl, and NaCl) and on the concentration fo the metal cation in the melt. An enhancement in Brønsted acidity of HCl is observed in the neutral buffered melts, although to a lesser degree than that in the acidic melts. A Hammett acidity function was determined for a NaCl (originally 55 mol % AlCl₃) buffered melt, $H_0 = -11.3.$, $H_0 = -12.7$ for a HCl (1 atm)/LiCl/AlCl₃:EMIC (originally 55 mol % AlCl₃) buffered melt.

Studies on the Acidity of Neutral Buffered 1-Ethyl-3-Methylimidazolium – AlCl₃ Ambient Temperature Molten Salts, Peter Koronaios, Dawn King, and Robert A. Osteryoung, Inorg. Chem. **37**, 2028-32 (1998). (Appendix A – Ref. 147)

Abstract: A series of studies on the acidity of AlCl₃-1-ethyl-3methylimidazolium chloride (EMIC) melts buffered with alkali metal chlorides were carried out. The solubility of HCl, a strong Brønsted acid in these melts, was measured in melts buffered with LiCl, NaCl, and KCl. The solubility of HCl in all three melts is 450 – 475 mM under 1 atm of HCl, approximately the same as that in the acidic (AlCl₃ rich) melts. The relative solubility products of LiCl, NaCl, and KCl were measured, and it was found that $K_{sp}(NaCl)/K_{sp}(LiCl) = 72 \pm 6$ and $K_{sp}(KCl)/K_{sp}(NaCl) = 1000 \pm 400$. It is likely that the differences in the acidity of HCl in the various melts are due to the differences in the solubility product of the relevant alkali metal chlorides. These ratios are consistent with the results of previous studies on the acidity of HCl in the melts. The concentrations of the strongly Lewis acidic Al₂Cl₂ ion in melts buffered with LiCl were measured using an aluminum electrode. The results of the potentiometric work indicate that a melt containing 1 M Li⁺ (approximately n_{AlCl_3} / n_{EMIC} R = 1.25:1 prior to buffering) would contain about 200uM Al₂Cl₇. This corresponds to a solubility product of about $(1.5 \pm 0/5) \times 10^{-12} \,\mathrm{M}^2$. The liquid junction potentials between unbuffered an buffered melts were found to be about 49 mV x ([Li[†][/M). These results are related to previous work on the acidity of

HCl in these melts, and it is shown that it is possible to explain many of the acidity and latent acidity results on the basis of the solubility products of the alkali metal chlorides.

Gutmann Acceptor Properties of LiCl, NaCl, and KCl Buffered Ambient Temperature Chloroaluminate Ionic Liquids, Robert A. Mantz, Paul C. Trulove, Richard T. Carlin, Terry L. Theim, and Robert A. Osteryoung, Inorg. Chem., 36, 1227-1232 (1997)

Abstract: Gutmann acceptor numbers have been determined using ³¹P nuclear magnetic resonance (NMR) for AlCl₃/EMIC melts as well as LiCl, NaCl and KCl neutral buffered melts. In AlCl₃/EMIC melts, where EMIC is 1-ethyl-3-methylimidazolium choride, the change in Gutmann acceptor number as a function of the AlCl₃-EMIC melt ratio is attributed to an equilbirum between a monoadduct of triethylphosphine oxide-AlCl₃ and a diadduct of triethylphosphine oxide-2AlCl₃. Observed acceptor numbers of the neutral buffered melts appears linear with respect to the melt's initial mole ratio of AlCl₃:EMIC prior to buffering. The lithium cation appears to be the most Lewis acidic alkali metal cation followed by the sodium and potassium cations. Possible reasons for the change in acceptor number as a function of changing alkali metal cation concentration are presented.

Buffered Chloroaluminate Melts and Latent Acidity, Robert A. Osteryoung, Proceedings of the Twelfth International Symposium on Molten Salts, P.C. Trulove, H. C. De Long, G. R. Stafford, and, Eds., Proceedings Volume, The Electrochemical Society, Pennington, NJ (2000), submitted for publication.

Abstract: Here we discuss the concept of latent acidity in neutral buffered chloroaluminate ionic liquids. Latent acidity involves a reaction between a weak organic base and a Lewis or Brønsted acid in a buffered chloroaluminate melt. The reactions are

B:
$$+ AICI_4^- + M^+ = B:AICI_3 + MCI(s)$$

 $+ HCI + B: + M^+ \rightarrow B:H^+ + MCI(s)$

where B: is an organic base that can form an aluminum chloride or protonated adduct, and M⁺ is an alkali metal (or alkaline earth) cation. Neither of these reactions will take place in basic or neutral, but unbuffered, melts. Both reactions are driven by the precipitation of the MCl(s), and the acidity depends on the alkali metal cation used, with the acidity increasing Li⁺>Na⁺>K⁺.

B. Speciation and Buffering Agents

Anodization and Speciation of Magnesium in Chloride-Rich Room-Temperature Ionic Liquids, Joan Fuller, Richard T. Carlin, Peter Koronaios, Robert Mantz, and Robert A. Osteryoung, J. Electrochem. Soc., 145, 24-28, (1998)

Abstract: Magnesium anodization was examined in room temperature AICI₃:EMIC and AICI₃:DMPIC ionic liquids, where EMIC – 1-ethyl-3methylimidazolium chloride and DMPIC – 1,2-dimethyl-3-propylimidazolium chloride. For All melts, the AlCl₃:organic chloride mole ratio was <1, yielding chloride-rich (i.e., basic) compositions. The rate of magnesium anodizatioin was limited by diffusion of chloride ions to the electrode surface. From the Cottrell slopes for magnesium anodization at a Mg disk electrode, and for chloride oxidation a a Pt disk electrode, the chloride stoichiometry of the anodization process in AlCl3:EMIC was determined to be 4.1 (± 0.5), corresponding to the formation of soluble MgCl₄²¹. Similar chloride stoichiometry was found in AICl₃:DMPIC. MqCl₂ buffers the melt to approximate neutrality from the basic side, dissolving as MgCl₄². Magnesium metal was chemically stable in basic AlCl₃:DMPIC, but it reacted completely and irreversibly with basic AICl₃:EMIC to produce colored organic byproducts. Some comments are made on the acidity of iCl2 and CdCl2 in the basic melts.

Alkaline Earth Chlorides as Buffering Agents for Ambient Temperature Chloroaluminate Molten Salts, Peter Koronaios and Robert A. Osteryoung, , Proceedings of Eleventh International Symposium on Molten Salts, P.C. Trulove, H. C. De Long, G. R. Stafford, and S. Deki, Eds., Proceedings Volume 98-11, pgs. 244-251, The Electrochemical Society, Pennington, NJ (1998)

Abstract: We have observed that it is possible to buffer 1-ethyl-3-methylimidazolium chloride (EMIC)-AICl₃ melts to neutrality using MgCl₂ or CaCl₂. CaCl₂ acts as a base buffering acidic (AICl₃ –rich) melts. The electrochemical wondow of both buffered melts is about 4.4V, the same as that of a neutral (equimolar) melt and wider than that of an acidic or basic melt. CaICl₂ buffers melts by forming the Ca²⁺ ion. CaCl₂-buffered melts have greater 'residual' acidity than melts buffered with alkali metal chlorides, as shown by potentiometric analysis with an Ag/AgCl electrode, and studies of the relative solubility products of LiCl and CaCl₂.

MgCl₂ byffers basic melts by taking up chloride ions to form the MgCl₄²⁻ion.

Behavior of Oxide Containing Chloroaluminate Molten Salts, Robert Mantz, Jack Summers, and Robert A. Osteryoung, Proceedings of the Eleventh International Symposium on Molten Salts, P.C. Trulove, H. C. De

Long, G. R. Stafford, and S. Deki, Eds., Proceedings Volume 98-11, pgs. 231-243, The Electrochemical Society, Pennington, NJ (1998)

Abstract: The role oxide and hydroxide species play in AlCl₃/1-ethyl-3-methylimidazolium chloride (EMIC) melts has been investigated. The oxide and hydroxide species are formed when water is introduced into the melts. Water is an ubiquitous impurity. Melts will be exposed to small amounts of water even when extreme precautions are taken. Both electrochemical and ¹⁷O NMR experiments were conducted in order to characterize the effect of oxides and hydroxides on melt properties. The presence of an aluminum hydroxide species causes the melt to behave as a neutral buffered melt. The degree of buffering increases as the hydroxide concentration increases.

CaCl₂ and MgCl₂ as Buffering Agents for Room-Temperature Chloroaluminate Ionic Liquids, Peter Koronaios and Robert A. Osteryoung, J. Electrochem. Soc., **146**, 2995 -2999 (1999).

Abstract: We have found that it is possible to buffer acidic 1-ethyl-3-methylimidazolium chloride (EMIC)/AICl₃ melts to neutrality using CaCl₂ as a buffering agen, while MgCl₂ will partially buffer acidic melts. The buffering reaciont is:

$$MCl_2(S) + 2Al_2Cl_7^- \rightarrow M^{2+} + 4AlCl_4^-$$

Where M is Ca or Mg. From studies using the Ag/AgCl electode as a chloride-sensitive electrode and from measurements of the relative solubility products of LiCl and CaCl₂, it appears that the residual concentration of the acidic Al₂Cl₇⁻ ion in the CaCl₂-buffered melts is significantly higher than in any of the other other neutral buffered melts studied so far, making this melt more acidic. Theses melts show the phenomenon known as "latent acidity," forming an AlCl₃ complex with the weak Lewis base acetylferrocene. When MgCl₂ is used as a buffering agent, the reaction above does not go to completion; it is explained in terms of the solubility product of MgCl₂.

Use of the Ag/AgCI/CI⁻ Electrode to Estimate Solubility Products in Ambient Temperature Ionic Liquids, Peter Koronaios and Robert A. Osteryoung, J. Electrochem Soc., submitted, December, 1999.

Abstract: The silver-silver chloride electrode has been investigated in 1-ethyl-3-methylimidazolium chloride aluminum chloride room temperature ionic liquids. It was found that the electrode is stable only in a narrow range of acidity around the neutral point, but in this range functions as a reversible Ag/AgCl/Cl⁻ system. The electrodes were used to make measurements in buffered and neutral buffered melts to estimate the solubility products (and complex formation constants) of several buffering agents; the solubility products are related to the acidity of the buffered neutral melts. In the case of melts buffered with LiCl, NaCl, and KCl,

the values of solubility products obtained were in accord with previous measurements where the ratio of solubility products was determined.

C. Non-Haloaluminate Ionic Liquids

The Room Temperature Ionic Liquid 1-Ethyl-3-Methylimidazolium Tetrafluorborate: Electrochemical Couples and Physical Properties, Joan Fuller, Richard Carlin, and Robert A. Osteryoung J. Electrochem. Soc., 144, 3881-3886 (1997)

Abstract: The room temperature ionic liquid 1-ethyl-3-methylimidazolium tetrafluoroborate (EMIBF₄) was demonstrated as a versatile electrolyte by examining three representative electrochemical couples, ferrocene and tetrathiafulvalene oxidations and lithium ion reduction. Square-wave voltammetric data for ferrocene oxidation were fit to a reversible one-electron process using the COOL algorithm to give a half-wave potential of 0.490V vs. Al/Al(IIII) and a diffusion coefficient of 5.1 x 10^{-7} cm² s⁻¹. The two-electron oxidation of tetrathiafulvalene was reversible and proceeded through two consecutive one-electron steps, although data collected at lower square-wave frequencies indicated a slow precipitation of the TTF species. Lithium ion was reduced to lithium metal at a Pt electrode following the addition of water to the EMIBF₄ electrolyte, whereas lithium ion reduction at an Al wire produced the β-LiAl alloy. Conductivities and kinematic viscosities of EMIBF_r were measured from 20 to 100 °C and had values of 14 mS cm⁻¹ and 0.275 cm² s⁻¹, respectively, at 25°C.

Diffusion Coefficients of Ferrocene in Composite Materials Containing Ambient Temperature Ionic Liquids, Marek Kosmulski, Robert A. Osteryoung, and Malgorzata Ciszkowska, J. Electrochem. Soc., in press.

Abstract: Diffusion coefficients of ferrocene in composite materials composed of the ambient temperature ionic liquids 1,2-dimethyl, 3-(1-propyl) imidazolium tetrafluoroborate (DMPI BF₄) or 1-ethyl-3-methylimidazolium tetrafluoroborate (EMI BF₄) and hexafluoropropylene – vinylidine fluoride copolymer were estimated using chronoamperometry. The values of D obtained with the composite materials based on DMPI BF₄ ranged from 1×10^{-13} to 2.5×10^{-12} m²s⁻¹ and depended on the composition and pretreatment of the composite material. The latter value is equal to the diffusion coefficient of ferrocene in liquid DMPI BF₄. The values obtained with the composite materials based on EMI BF₄ ranged from 2×10^{-13} to 9×10^{-12} m²s⁻¹ and they are lower by a factor of more than four than that of ferrocene in liquid EMI BF₄.

III. Personnel

Senior Research Personnel

Dr. Boris Ravdel

Dr. Marek Kosmulski

Dr. Peter Koronaios

Jurnior Research Personnwl

Ms. Dawn King*
Capt. Robert Mantz**

^{*}M.S. received July, 1996
**Not paid on Contract funds; Ph.D. received February 1997.

APPENDIX A

Publications--Grant Related Activity - since AFOSR support initiated.

AFOSR-71-1955; 1 Jan. 1971 - 28 Feb. 1975

- Janet Osteryoung and R. A. Osteryoung, "The Advantage of Charge Measurements for Determining Kinetic Parameters", Electrochimica Acta, 16, 525 (1971).
- 2. R. A. Osteryoung, "Introduction to the On-Line Use of Computers in Electrochemistry", Vol. II, "Application of Computers to Chemical Instrumentation", Ed. by Mattson, Mark and MacDonald, Marcel Dekker (1973).
- 3. L. G. Boxall, H. L. Jones and R. A. Osteryoung, "Solvent Equilibria in AlCl₃-NaCl Melts", J. Electrochem. Soc., <u>120(2)</u>, 223 (1973).
- 4. H. Lloyd Jones, L. G. Boxall and R. A. Osteryoung, "Organic Electrode Reactions in Fused AlCl₃ Containing Solvents", J. Electroanal. Chem., <u>38</u>, 476 (1972).
- 5. L. G. Boxall, H. L. Jones and R. A. Osteryoung, "Electrochemical Studies on Ag, Fe and Cu Species in AlCl₃-NaCl Melts", J. Electroanal. Chem., 121, 212 (1974).
- 6. H. Lloyd Jones and R. A. Osteryoung, "Electrode Reactions of Aromatic Amines in Solvents Containing Fused AlCl₃:II.", J. Electroanal. Chem., 49, 281 (1974).
- 7. R. J. Gale and R. A. Osteryoung, "Investigation of Subvalent Ion Effects During Aluminum Anodization in Molten NaCl-AlCl₃ Solvents", J. Electrochem. Soc., <u>121</u>, 983 (1974).
- 8. V. R. Koch, L. L. Miller and R. A. Osteryoung, "Reductive Defunctionalization of 1-substituted Adamantanes in Molten Sodium Tetrachloroaluminate", J. Org. Chem., 39, 2416 (1974).
- H. Lloyd Jones and R. A. Osteryoung, "Organic Reactions in Molten Tetrachloroaluminate Solvents", Advances in Molten Salt Chemistry, Vol. 3, Edited by J. Braunstein, G. P. Smith and G. Mamantov, Plenum Publishing (1975).

- 10. R. J. Gale and R. A. Osteryoung, "Dissociative Chlorination of Nitrogen Oxides and Oxyanions in Molten Sodium Chloride-Aluminum Chloride Solvent", Inorg. Chem., 14, 1232 (1975).
- 11. H. L. Chum, V. R. Koch, L. L. Miller and R. A. Osteryoung, "An Electrochemical Scrutiny of Organometallic Iron Complexes and Hexamethylbenzene in a Room Temperature Molten Salt", J. Am. Chem. Soc., 97, 3264 (1975).
- 12. D.E. Bartak and R. A. Osteryoung, "The Electrochemical Oxidation of N,N,N',N'-Tetramethylbenzidine in Molten Sodium Tetrachloroaluminate", J. Electrochem. Soc., 122, 600 (1975).
- 13. J. Phillips, R. J. Gale, R. G. Wier and R. A. Osteryoung, "Glassy Carbon Rotating Ring-Disc Electrodes for Molten Salt Studies", Anal Chem., 48, 1266 (1976).
- 14. D. E. Bartak and R. A. Osteryoung, "The Redox Behavior of Tetrachloro-p-Benzoquinone-Tetrachlorohydroquinone Systems in Molten Aluminum Chloride-Sodium Chloride Solvents", J. Electroanal. Chem., <u>74</u>, 69 (1976).

AFOSR 75-2776; 1 March 1975 - 31 May 1976

- 15. V. R. Koch, L. L. Miller and R. A. Osteryoung, "Electroinitiated Friedel-Crafts Transalkylations in a Room Temperature Molten Salt Media", J. Am. Chem. Soc., <u>98</u>, 5377 (1976).
- 16. K. A. Paulsen and R. A. Osteryoung, "Electrochemical Studies on Sulfur and Sulfides in AlCl₃-NaCl Melts", J. Am. Chem. Soc. <u>,98</u>, 6866 (1976).
- 17. R. A. Osteryoung, "Chemistry and Electrochemistry in Aluminum Chloride Molten Salt Systems", Proceedings of the Symposium on Molten Salts, edited by J. P. Pemsler, J. Braunstein, K. Nobe, D. R. Morris, pp. 240-253, The Electrochemical Society, Pennington, NJ (1976).

AFOSR 766-2978; I April 1976 - 30 June, 1979

- 18. J. Phillips and R. A. Osteryoung, "Molybdenum Chemistry in NaCl-AlCl₃ Melts at 175°C", J. Electrochem. Soc., <u>124</u>, 1405 (1977).
- 19. J. Robinson, B. Gilbert and R. A. Osteryoung, "The Acid-Base Chemistry of Oxide and Chalcogenides in Sodium Tetrachloroaluminate Melts at 175°C", Inorg. Chem., <u>16</u>, 3040 (1977).

- 20. Helena Li Chum, T. Rabockai, J. Phillips and R. A. Osteryoung, "Ligand Oxidation in Iron Diimine Complexes. III. Electrochemical Oxidation of tris-(glyoxalbis(methylimine))Iron(II)", Inorg. Chem., <u>16</u>, 1812 (1977).
- 21. Helena Li Chum, D. Koran and R. A. Osteryoung, "The Electrochemical Behavior of Metal Carbonyls in a Mixture of a Room Temperature Molten Salt and Benzene", J. Organometallic Chem., 140, 349 (1977).
- 22. Helena Li Chum, D. Koran and R. A. Osteryoung, "Photochemistry of Iron(II)Diimine Complexes in a Room Temperature Molten Salt", J. Am. Chem. Soc., 100, 310 (1978).
- 23. J. Robinson and R. A. Osteryoung, "Electrochemical Studies of Selenium and Selenium Compounds in Molten Sodium Tetrachloroaluminate Melts", J. Electrochem. Soc., 125, 1454 (1978).
- 24. B. Gilbert and R. A. Osteryoung, "Electrochemical Studies on Nickel Electrodes in Molten Sodium Tetrachloroaluminates", J. Am. Chem. Soc., 100, 2725 (1978).
- 25. Gleb Mamantov and R. A. Osteryoung, "Acid-Base Dependent Redox Chemistry in Molten Chloroaluminates", in "Characterization Or Solutes in Non-Aqueous Solutions", pg 225-250, G. Mamantov, Ed., Plenum Publishing Co. (1977).
- 26. R. J. Gale, B. Gilbert and R. A. Osteryoung, "Raman Spectra of Molten Aluminum Chloride: 1 Butylpyridinium Chloride Systems at Ambient Temperature", Inorg. Chem., 17, 2728 ~978).
- 27. J. Robinson and R. A. Osteryoung, "The Electrochemical Behavior of Te(IV) in Sodium Tetrachloroaluminates", J. Electrochem. Soc., <u>125</u>, 1784 (1978).
- 28. J. Robinson and R. A. Osteryoung, "The Electrochemical and Spectroscopic Behavior of Some Aromatic Hydrocarbons in the Room Temperature Molten Salt System AlCl₃:n-Butylpyridinium Chloride", J. Am. Chem. Soc., 101, 321 (1978).
- 29. J. Robinson, R. C. Bugle, H. L. Chum, D. Koran and R. A. Osteryoung, ¹H and ¹³C Nuclear Magnetic Resonance Spectroscopy Studies of Aluminum Halide-Alkyl Pyridinium Halide Molten Salts and Their Benzene Solutions", J. Am. Chem. Soc, <u>101</u>, 3776 (1979).
- 30. R. J. Gale and R. A. Osteryoung, "Potentiometric Investigation of Dialuminum Heptachloride Formation in Aluminum Chloride: 1-butyl-pyridinium Chloride Mixtures", Inorg. Chem., <u>18</u>, 1603 (1979).

AFOSR F49620-79-C-0142: 1 June 1979 - 30 Sept. 1980

- 31. J. Robinson and R. A. Osteryoung, "The Electrochemical Behavior of Aluminum in the Low Temperature Molten Salt System n-Butyl Pyridinium Chloride; Aluminum Chloride and Mixtures of this Molten Salt with Benzene", J. Electrochem. Soc., 127, 122 (1980).
- 32. J. Robinson and R. A. Osteryoung, "An Investigation into the Electrochemical Oxidation of Some Aromatic Amines in the Room Temperature Molten Salt System AlCl₃:N-Butylpyridinium Chloride", J. Am. Chem. Soc., 102, 4415 (1980).
- 33. R. J. Gale and R. A. Osteryoung, "Electrochemical Reduction of Pyridinium Ions in Ionic Aluminum Chloride-Alkylpyridinium Halide Ambient Temperature Liquids", J. Electrochem.Soc., <u>127</u>, 2167 (1980).
- 34. R. J. Gale and R. A. Osteryoung, "Electrical Double Layer at Mercury in Room Temperature Aluminum Chloride- Butylpyridinium Chloride Ionic Liquids", Electrochemica Acta, <u>25</u>, 1527 (1980).
- 35. R. J. Gale and R. A. Osteryoung, "Infrared Spectral Investigations of Ambient Molten Aluminum Chloride:-1-Butylpyridinium Chloride Systems", Inorg. Chem., 19, 2240 (1980).
- 36. Janet Osteryoung and Emilia Kirowa-Eisner, "Reverse Pulse Polarography", Anal. Chem., 52, 62-66 (1980).
- 37. Koichi Aoki, R. A. Osteryoung and Janet Osteryoung, "Differential Normal Pulse Voltammetry", J. Electroanal. Chem., <u>110</u>, 1-18 (1980).

AFOSR-81-0007; 1 October, 1980 - 31 August, 1984

- 38. B. J. Welch and R. A. Osteryoung, "Electrochemical Studies in Low Temperature Molten Salt Systems Containing Aluminum Chlorides", J. Electroanal. Chem., <u>118</u>, 455-466 (1981).
- 39. Z. StoJek, H. Linga and R. A. Osteryoung, "A Titration Procedure for the Determination of Oxide in Basic n-Butylpyridinium Chloride: Aluminum Chloride Melts", J. Electroanal. Chem., <u>119</u>, 365-70 (1981).
- 40. H. Linga, Z. Stojek and R. A. Osteryoung, "Electrochemistry of Titanium(III) in Basic n-Butylpyridinium Chloride and Aluminum Chloride in Presence of Oxide", J. Am. Chem. Soc., <u>103</u>, 3754 (1981).

- 41. Helena Li Chum, D. Koran and R. A. Osteryoung, "Substituent Effects in Iron Diimine Complexes: Correlations with Thermodynamic Properties in a Room Temperature Molten Salt", Inorg. Chem., 20, 3304-3307 (1981).
- *42. T. R. Brumleve, John J. O'Dea, Robert Osteryoung and Janet Osteryoung, "Differential Normal Pulse Voltammetry in the Alternate Pulse Mode Reversible Electrode Reactions", Anal. Chem., 53, 702 (1981).
- *43. T. R. Brumleve and Janet Osteryoung, "Theory of Differential Normal Pulse Voltammetry in the Alternating Pulse Mode for Totally Irreversible Electrode Reactions", Anal. Chem., <u>53</u>, 988-991 (1981).
- *44. T. R. Brumleve, R. A. Osteryoung and Janet Osteryoung, "Differential Normal Pulse Voltammetry for the Anodic Oxidation of Iron(II); Anal. Chem., 54, 782-787 (1982).
- *45. T. R. Brumleve and Janet Osteryoung, "Spherical Diffusion and Shielding Effects in Reverse Pulse Voltammetry", J. Phys. Chem., <u>86</u>, 1794-1801 (1982).
- 46. G. T. Cheek and R. A. Osteryoung, "Electrochemical and Spectroscopic Studies of 9,10-Anthraquinone in a Room Temperature Molten Salt", J. Electrochem. Soc., <u>129</u>, 2488 (1982).
- 47. C. Nanjundiah, K. Shimizu and R. A. Osteryoung, "Electrochemical Studies of Fe(II) and Fe(III) in an Aluminum Chloride-Butylpyridinium Chloride Ionic Liquid", J. Electrochem. Soc., 129, 2474 (1982).
- 48. G. T. Cheek and R. A. Osteryoung, "Preparation and Characterization of a Substituted Alkylpyridinium Chloroaluminate Molten Salt System", Inorg. Chem., <u>21</u>, 3581 (1982).
- 49. G. T. Cheek and R. A. Osteryoung, "An Electrochemical and Infra-red Study of Chloranil in n-Butylpyridinium Chloride:Aluminum Chloride Ionic Liquid", J. Electrochem. Soc., <u>129</u>, 2739 (1982).
- Chenniah Nanjundiah and R. A. Osteryoung, "Electrochemical Studies of Cu(I) and Cu(II) in an Aluminum Chloride-N-(n-Butylpyridinium) Chloride Ionic Liquid", J. Electrochem. Soc., <u>130</u>, 1312 (1983).
- 51. Saeed Sahami and R. A. Osteryoung, "Voltammetric Determination of Water in an Aluminum Chloride-N-n-Butylpyridinium Chloride Ionic Liquid", Anal. Chem., <u>55</u>, 1970 (1983).

*Work related to pulse methodology development but not supported by A.F.O.S.R.

- 52. Z. Karpinski and R. A. Osteryoung, "Electrochemical Studies of Iodine in an Aluminum Chloride-Butylpyridinium Chloride Ionic Liquid. I. Acidic Solvent Composition", J. Electroanal. Chem., 164, 281 (1984).
- 53. D. A. Habboush and R. A. Osteryoung, "Electrochemical Studies of Sb(III) and Sb(V) in Molten Mixtures of Aluminum Chloride and Butylpyridinium Chloride", Inorg. Chem., 23, 1726 (1984).
- 54. R. A. Osteryoung, R. J. Gale, J. Robinson, R. Bugle and B. Gilbert, "Electrochemical Studies in Room Temperature Molten Salts", in "Proceedings of the Second International Symposium on Molten Salts", J. Braunstein and R. Selman, eds., pg. 214-219, The Electrochemical Society, Pennington, NJ (1981).
- 55. R. A. Osteryoung, G. Cheek and H. Linga, "Studies in Room Temperature Chloroaluminates", in "Proceedings of the Third International Symposium on Molten Salts", G. Mamantov, ed., pg. 221-236, The Electrochemical Society, Pennington, NJ (1981).
- 56. C. Nanjundiah, K. Shimizu and R. A. Osteryoung, "Electrochemical Studies in an Aluminum Chloride-Butylpyridnium Chloride Ionic Liquid" in "Proceedings of the Workshop on Thermally Regenerative Electrochemical Systems", SERI/CP-234-1577, Solar Energy Research Institute, Golden, Colorado (1982).
- 57. H. L. Chum and R. A. Osteryoung, "Chemical and Electrochemical Studies in Room Temperature Aluminum Halide Containing Melts", in "Ionic Liquids", D. Inman and D. Lovering, eds., pg. 407-423, Plenum Press, London (1981).
- 58. R. J. Gale and R. A. Osteryoung, "High and Room Temperature Haloalumintes", in "Molten Salt Techniques", D. Lovering and R. J. Gale, eds., Ch. 3, pgs 55-78, Plenum Press, New York (1983).
- 59. G. T. Cheek and R. A. Osteryoung, "Preparation and Characterization of a Substituted Alkylpyridinium Chloroaluminate Molten Salt System", Inorg. Chem., 21, 3581 (1982).
- 60. M. Lipsztajn and R. A. Osteryoung, "Increased Electrochemical Window in Ambient Temperature Ionic Ionic Liquids", J. Electrochem. Soc., <u>130</u>, 1968 (1983).
- 61. M. Lipsztajn and R. A. Osteryoung, "Reactions of Chloride Ions in Low Temperature Molten Salt and Applications to the Study of Complex Ion Stoichiometry", Inorg. Chem., 23, 1735 (1984).

- Z. Karpinski and R. A. Osteryoung, "On Determination of Equilibrium Constants for the Tetrachloroaluminate Dissociation in Ambient Temperature Ionic Liquids", Inorg. Chem., <u>23</u>, 1491 (1984).
- 63. P. G. Pickup and R. A. Osteryoung, "Polymer Coated Electrodes in Ambient Temperature Ionic Liquids", J. Electrochem. Soc., <u>130</u>, 1965 (1983).
- 64. S. Sahami and R. A. Osteryoung, "Electrochemical and Spectroscopic Studies of Polypyridine Complexes of Fe(II)/(III) and Ru(II)/(III) in the Aluminum Chloride N-(1-Butyl)pyridinium Chloride Molten Salt System", Inorg. Chem., 23, 2511 (1984).
- 65. P. G. Pickup and R. A. Osteryoung, "Electrochemical Polymerization of Pyrrole and Electrochemistry of Polypyrrole Films in Ambient Temperature Molten Salts", J. Am. Chem. Soc., <u>106</u>, 2294 (1984).

AFOSR-84-0292; 1 August 1984 - 30 November 1986

- 66. P. G. Pickup and Robert A. Osteryoung, Charging and Discharging Rate Studies of Polypyrrole Films in AlCl₃:1-Methyl-(3-Ethyl)-Imidazolium Chloride Molten Salts and in CH₃CN" J. Electroanal. Chem., <u>195</u>, 271 (1985).
- 67. P. G. Pickup and Robert A. Osteryoung, Charge Transport in Poly-[Ru(2,2'-Bipyridine) (4-Vinylpyridine)]^{3+/2+} Films in AlCl₃ /N-(1-Butyl)pyridinium Chloride and AlCl₃ /1-Methyl(3-Ethyl)imidazolium Chloride Molten Salts" J. Electroanal. Chem., <u>186</u>, 99 (1985).
- 68. P. G. Pickup and R. A. Osteryoung, "Electrochemistry and Spectroelectrochemistry in CH₃CN and Aluminum Chloride/N-(1-Butyl)pyridinium Chloride Molten Salts of Films Prepared by Electrochemical Polymerization of Tris(5-amino-1,10-phenanthroline)Iron (II)", Inorg. Chem., 24, 2707 (1985).
- 69. L. Janiszewska and R. A. Osteryoung, "Electrochemistry of Polythiophene and Polybithiophene Films in Ambient Temperature Molten Salts", J. Electrochem. Soc., <u>134</u>, 2787 (1987).
- 70. M. LipsztaJn and R. A. Osteryoung, "Electrochemical Reduction of N-(1-Butyl)Pyridinium Cation in 1-Methyl-3-Ethyl-Imidazolium Chloride-Aluminum Chloride Ambient Temperature Ionic Liquids", Electrochim. Acta, 29, 1349 (1984).

- 71. M. LipsztaJn and R. A. Osteryoung, "Electrochemistry in Neutral Ambient Temperature Ionic Liquids. Part I. Studies of Iron(III), Neodymium(III) and Lithium(I)", Inorg. Chem., <u>24</u>, 716 (1985).
- 72. M. Lipsztajn and R. A. Osteryoung, "Studies of Antimony(III) in Ambient Temperature Ionic Liquids", Inorg. Chem., <u>24</u>, 3492 (1985).
- 73. M. Lipsztajn, S. Sahami and R. A. Osteryoung, "Hydroquinone as a Proton Donor in Ambient Temperature Chloroaluminate Ionic Liquids: Reaction with Chloride Ion", Inorg. Chem., <u>25</u>, 549 (1986).
- 74. Z. Karpinski, C. Nanjundiah and R. A. Osteryoung, "Electrochemical Studies of Ferrocene and Ferrocenium Ion in Liquid", Inorg. Chem., <u>23</u>, 3358 (1984).
- 75. Z. Karpinski and R. A. Osteryoung, "Electrochemical Studies of Iodine in an Aluminum Chloride-Butylpyridinium Chloride Ionic Liquid: Part II. Neutral and Basic Solvent Composition", J. Electroanal. Chem., <u>178</u>, 281 (1984).
- 76. Z. Karpinski and R. A. Osteryoung, "Spectrophotometric Studies of Iodine Complexes in an Aluminum Chloride-Butylpyridinium Chloride Ionic Liquid", Inorg. Chem., 23, 4561 (1984).
- 77. Z. Karpinski and R. A. Osteryoung, "Potentiometric Studies of the Chlorine Electrode in Ambient Temperature Chloroaluminate Ionic Liquids: Determination of Equilibrium Constants for Tetrachloroaluminate Ionic Dissociation", Inorg. Chem., 24, 2259 (1985).
- 78. S. Sahami and R. A. Osteryoung, "Electrochemical Oxidation of Some Metal Carbonyls in Ambient Temperature Ionic Liquids", Electrochim. Acta, 30, 143 (1985).
- 79. M. Lipsztajn and R. A. Osteryoung, "On Ionic Association in Ambient Temperature Chloroaluminate Molten Salts: Analysis of Electrochemical and Conductance Data", J. Electrochem. Soc., <u>132</u>, 1126 (1985).
- 80. T. A. Zawodzinski, Jr., R. Kurland and R. A. Osteryoung, "Relaxation Time Measurements in N-(1-Butyl)pyridinium-Aluminum Chloride Ambient Temperature Ionic Liquids", J. Phys. Chem., 91, 962 (1987).
- 81. Robert A. Osteryoung, "Organic Chloroaluminate Ambient Temperature Molten Salts" in Molten Salt Chemistry: An Introduction and Selected Applications, G. Mamantov and R. Marassi, Eds., Pgs. 329-364, NATO ASI Series C: Mathematical and Physical Sciences, Vol. 202, D. Reidel Publishing Co., Dordrecht, Boston, (1987).

AFOSR-87-0088; 1 December, 1986 - 30 November, 1989

- 82. T. A. Zawodzinski, Jr. and R. A. Osteryoung, "Aspects of the Chemistry of Water in Ambient Temperature Chloroaluminate Ionic Liquids: ¹⁷0 NMR Studies", Inorg. Chem., <u>26</u>, 2920 (1987).
- 83. T. A. Zawodzinski, Jr. and R. A. Osteryoung, "The Chemistry of Water in Ambient Temperature Chloroaluminate Ionic Liquids: NMR Studies" in Proceedings of the Joint International Symposium on Molten Salts, G. Mamantov et al., Eds., Vol. 87-7, pp. 406-413, The Electrochemical Society, Pennington, NJ (1987).
- 84. T. A. Zawodzinski, Jr., R. Carlin and R. A. Osteryoung, "Removal of Protons from Chloroaluminate Ionic Liquids", Anal. Chem., <u>59</u>, 2639 (1987).
- 85. L. Janiszewska and R. A. Osteryoung, "Investigations on the Formation of Polyfluorene and Its Electrochemistry in Ambient Temperature Ionic Liquids", J. Electrochem. Soc., <u>135</u>, 116 (1988).
- 86. F. Uribe and R. A. Osteryoung, "Electrochemical and Spectroscopic Studies of 1,4-Benzoquinone in Ambient Temperature Chloroaluminate Molten Salts", J. Electrochem. Soc., <u>135</u>, 378 (1988).
- 87. J. F. Oudard, R. Allendoerfer and R. A. Osteryoung, "Simultaneous EPR Electrochemical and Spectroscopic Studies in Ambient Temperature Ionic Liquids", J. Electroanal. and Interfac. Chem., <u>241</u>, 231 (1988).
- 88. J. F. Oudard, R. Allendoerfer and R. A. Osteryoung, "Simultaneous EPR Electrochemical Measurements on Polyfluorene in Ambient Temperature Ionic Liquids", Synth. Met., 22, 407 (1988).
- 89. R. Carlin and R. A. Osteryoung, "Electrochemistry of Molybdenum Chloride Dimers in a Basic Ambient Temperature Molten Salt", Inorg. Chem., <u>27</u>, 1483 (1988).
- 90. Lin Sinru, J. J. O'Dea, J. Osteryoung and R. A. Osteryoung, "Normal and Reverse Pulse Voltammetry at Microdisc Electrodes", Anal. Chem., <u>60</u>, 1135 (1988).
- 91. Lin Sinru and R. A. Osteryoung, "Normal and Reverse Pulse Voltammetry from Poised Systems at Microdisk Electrodes", Anal. Chem., <u>60</u>, 1845 (1988).

- 92. R. Carlin and R. A. Osteryoung, "Reactions of Protons and Molybdenum Dimers in an Ambient Temperature Molten Salt", Inorg. Chem., <u>27</u>, 3675 (1988).
- 93. R. Carlin and R. A. Osteryoung, "Microelectrodes in the Examination of Anodic and Cathodic Limit Reactions of an Ambient Temperature Molten Salt", J. Electroanal. and Interfac. Chem., <u>252</u>, 81 (1988).
- 94. T. A. Zawodzinski, Jr. and R. A. Osteryoung, "1-Methyl-3-Ethylimidazolium Hydrogen Bichloride: Synthesis and Application to the Study of Protons in Ambient Temperature Chloroaluminate Ionic Liquids", Inorg. Chem., <u>27</u>, 4383 (1988).
- 95. T. A. Zawodzinski, Jr., L. Janiszewska and R. A. Osteryoung, "On the Chemistry of Pyrrole in Room Temperature Chloroaluminate Melts", J. Electroanal. and Interfac. Chem., 255, 111, (1988).
- 96. B. Das, R. T. Carlin and R. A. Osteryoung, "The Ferro/Ferricyanide Couple in Aluminum Chloride-Imidazolum Chloride Ambient Temperature Molten Salts", Inorg. Chem., <u>28</u>, 421 (1989).
- 97. T. A. Zawodzinski, Jr. and R. A. Osteryoung, "Donor-Acceptor Properties of Ambient Temperature Chloroaluminate Melts", Inorg. Chem., <u>28</u>, 1710 (1989).
- *98. R. Carlin and R. A. Osteryoung, "Aluminum Anodization in Basic Ambient Temperature Molten Salts", J. Electrochem. Soc., 136, 1409 (1989).

AFOSR 90-0099; 1 December, 1989 - 30 June, 1992

- *99. R. T. Carlin and R. A. Osteryoung, "Deposition Studies of Lithium and Bismuth at Tungsten Microelectrodes in LiCl:KCI Eutectic", J. Electrochem. Soc., 136, 1249-1255 (1989).
- 100. Thomas A. Zawodzinski, Jr. and R. A. Osteryoung, "Donor Acceptor Properties of Ambient-Temperature Chloroaluminate Melts", Inorg. Chem., 28,1710-1715 (1989).
- 101. P. C. Trulove, R. T. Carlin, and R. A. Osteryoung, "Lewis and Bronsted Acid Adducts in Ambient Temperature Chloroaluminate Molten Salts", J. Am. Chem. Soc., 112, 45674568 (1990).
- 102. Marc A.-M. Nöel and Robert A. Osteryoung, "Determination of the Stoichiometry of Some Metal Chlorocomplex Ions in Basic Ambient Temperature Molten Salts", J. Electroanal. Chem., <u>284</u>, 413-429 (1990).
- * Work relevant to this grant but supported in part by SDIO/IST, managed by ONR.

- 103. Thomas A. Zawodzinski, Jr. and R. A. Osteryoung, "Oxide and Hydroxide Species Formed on Addition of Water in Ambient Temperature Chloroaluminate Melts: An ¹⁷0 NMR Study", Inorg. Chem., <u>29</u>, 2842-2847 (1990).
- 104. R. T. Carlin, R. A. Osteryoung, J. S. Wilkes and J. Rovang, "Studies of Titanium(IV) Chloride in a Strongly Lewis Acidic Molten Salt: Electrochemistry, Titanium NMR and Electronic Spectroscopy", Inorg. Chem., 29, 3003-3009 (1990).
- 105. Marc Nöel and R. A. Osteryoung, "Use of Metal Chlorides to Buffer Neutral Ambient Temperature Molten Salts", J. Electroanal. Chem., <u>293</u>, 108, 139-150 (1990).
- 106. Basudev K. Das and Robert A. Osteryoung, Electrochemistry of 9,10-Anthraquinone Moiety of [1-Pyrrol-1-YL) -HEX-6-YL]-9,10-Anthraquinone-2-Sulfonate in Aluminum Chloride-1-Methyl-3-Ethylimidazolium Chloride Ambient Temperature Melt, J. Bangladesh Chem. Soc., 3(2), 147-152 (1990).
- 107. Soo-Gil Park, Paul C. Trulove, Richard T. Carlin and Robert A. Osteryoung, "A Mixed Lewis Acid-Bronsted Acid Ambient Temperature Ionic Liquid: An Electrochemical and NMR Study of Dimethylaniline", J. Am. Chem. Soc., 113, 3334-3340 (1991).
- 108. Michael T. Carter, Charles L. Hussey, S. K.D. Strubinger, and Robert A. Osteryoung, "Electrochemical Reduction of Dioxygen in Room-Temperature Imidazolium Chloride-Aluminum Chloride Molten Salts", Inorg. Chem., 30, 1149-1151 (1991).
- *109. Renewal of Boundary Conditions in Pulse Voltammetry at Microdisk Electrodes for Non-Reversible Systems, Z. J. Karpinski and Robert A. Osteryoung, J. Electroanal. Chem., 307, 47-62 (1991).
- 110. J. Tang and R. A. Osteryoung, "Electrochemistry of Polyaniline in Ambient Temperature Molten Salts: I", Syn. Met., <u>44</u>, 307-319 (1991).
- 111. J. Tang and R. A. Osteryoung, "Formation and Electrochemistry of Polyaniline in Ambient Temperature Molten Salts", .Syn. Met., <u>45</u>, 1-13 (1991).
- * Work relevant to this grant but supported in part by NSF

- 112. P. Trulove, M. Noel and R. A. Osteryoung, "Removal of Protons from Ambient-Temperature Chloroaluminate Ionic Liquids", Anal. Chem., 63, 2892-2896 (1991).
- 113. Marc A.M. Noel, R. Allendoerfer, and R. A. Osteryoung, "Solvation in Ionic Liquids: An EPR Study", J. Phys. Chem., 96, 2391-2394 (1992).
- 114. J. Tang, R. Allendoerfer and R. A. Osteryoung, "Simultaneous EPR and Electrochemical Measurements on Polyaniline in Ambient Temperature Molten Salts", J. Phys. Chem., <u>96</u>, 3531-3536 (1992).
- 115. Marc A.M. Noel, John J. O'Dea, and R. A. Osteryoung, "Short Time Pulse Voltammetry at Very Small Electrodes in Ambient Temperature Chloroaluminate Ionic Liquids", J. Electrochem. Soc., <u>139</u>, 1231 -1236 (1992).
- P. C. Trulove, R. T. Carlin and R. A. Osteryoung, "Interaction of Protons with Solutes in Ambient Temperature Chloroaluminate Molten Salts: Electrochemistry and NMR Spectroscopy of Protonated Anthracene", Proceedings of the Seventh International Symposium on Molten Salts, C. L. Hussey, S. N. Flengas, J. S.Wilkes and Y. Ito, Eds, The Electrochemical Society, Proceedings Volume 90-17, pgs. 306-324, Pennington, NJ (1990).
- 117. S. G. Park, P. Trulove, R. T. Carlin and R. A. Osteryoung, "Protons in Ambient Temperature Chloroaluminate Molten Salts: Electrochemical and NMR Studies of Their Interaction with Dimethylaniline", Proceedings of the Seventh International Symposium on Molten Salts, C. L. Hussey, S. N. Flengas, J. S. Wilkes and Y. Ito, Eds, The Electrochemical Society, Proceedings Volume 90-17, pgs. 290-305, Pennington, NJ (1990).
- Michael T. Carter and Robert A. Osteryoung, "Electrochemistry of 9,10-Anthraquinone in the Presence of Proton and Tetrachloroaluminate in Ambient Temperature Molten Salts", Proceedings of Eighth International Symposium on Molten Salts, R. J. Gale, George Blomgren, and H. Kojima, Eds., The Electrochemical Society, Proceedings Volume 92-16, pgs. 406-425, Pennington, NJ, (1992).
- 119. Paul C. Trulove and Robert A. Osteryoung, "The Nature of Proton in Ambient-Temperature Chloroaluminate Molten Salts", Proceedings of Eighth International Symposium on Molten Salts, R. J. Gale, George Blomgren, and H. Kojima, Eds., Proceedings Volume 92-16, pgs. 292-302, The Electrochemical Society, Pennington, NJ, (1992).
- 120. Paul C. Trulove and Robert A. Osteryoung, "The Chemistry of Proton in Ambient Temperature Chloroaluminate Molten Salts", Proceedings of Eighth International Symposium on Molten Salts, R. J. Gale, George Blomgren, and H. Kojima, Eds., Proceedings Volume 92-16, pgs. 303-316, The Electrochemical Society, Pennington, NJ, (1992).

AFOSR Grant F49620-92-J-0326: 1 July, 1992 - 31 December, 1993

- 121. Richard Carlin, Paul Trulove and Robert A. Osteryoung, "Electrochemical and Spectroscopic Study of Anthracene in a Mixed Lewis-Brønsted Acid Ambient Temperature Molten Salt System", Electrochim. Acta, <u>37</u>, 2615-2628 (1992).
- 122. Jinsong Tang, Kunio Shimizu and Robert A. Osteryoung, "Electrochemical Studies of Tris-(acetylacetonato)ruthenium(III) Complex in Ambient Temperature Chloroaluminate Molten Salts", Inorg. Chem., 31, 3980-3985 (1992).
- Michael Carter and Robert A. Osteryoung, "Interaction of 9,10-Anthraquinone with Tetrachloroaluminate and Proton in Basic Aluminum Chloride:1-Ethyl-3-Methylimidazolium Chloride Room Temperature Molten Salts", J. Electrochem. Soc., <u>139</u>, 1795-1802 (1992).
- Paul C. Trulove and Robert A. Osteryoung, "Proton Speciation in Ambient Temperature Chloroaluminate Ionic Liquids, Inorg. Chem., 31, 3980-3985 (1992).
- 125. Paul C. Trulove, Dinesh K. Sukumaran, and Robert A. Osteryoung, "NMR Studies of the Proton Equilibrium in Basic Ambient-Temperature Chloroaluminate Ionic Liquids", Inorg. Chem., <u>32</u>, 4396 (1993).
- S. Song, J. Tang, M. Kajitani, K. Shimizu, and Robert A. Osteryoung, "Electrode Processes of (η⁵–Cyclopentadienyl)-(1,2-Substituted 1,2 Ethylenedithiolato)Cobalt(III) Complexes in an Ambient Temperature Molten Salt", J.. Chem., <u>455</u>, 211-217 (1993).
- 127 Richard T. Carlin and Robert A. Osteryoung, "A Silane-Based Electroactive Film Prepared in Imidazolium Chloroaluminate Molten Salt", J. Electrochem. Soc., **141** 1709-1713 (1994).
- 128. Z. J. Karpinski, S. Song and R. A. Osteryoung, "Dependence of Electron Transfer Kinetics of the Ferrocene/Ferrocenium Couple on the Viscosity in Ambient Temperature Chloroaluminate Ionic Liquids", Inorg. Chim. Acta, **225**, 9-14 (1994).
- 129. Leonid Goldenberg and Robert A. Osteryoung, "Benzene Polymerization in 1-Ethyl-3-Methylimidazolium Chloride-AlCl₃ Ionic Liquid", Syn. Met., **64**, 63-68 (1994).

AFOSR Contract F49620-94-1-0056, 1 January, 1994 - 30 June, 1996.

- 130. Michael T. Carter and Robert A. Osteryoung, "Heterogeneous and Homogeneous Electron Transfer Reactions of Tetrathafulvalene in Ambient Temperature Chloraluminate Molten Salts", J. Electrochem. Soc., 141, 1713-1720 (1994).
- I. C. Quarmby, R. A. Mantz, L. M. Goldenberg, and R. A. Osteryoung, "Examination of the Stoichiometry of Latent Acidity in Buffered Chloroaluminate Ionic Liquids", Anal. Chem. <u>,66</u>, 3558-3561 (1994).
- 132. I. C. Quarmby, R. A. Mantz, L. M. Goldenberg, and R. A. Osteryoung, "Latent Acidity in Buffered Chloroaluminate Ionic Liquids", Proceedings of Ninth International Symposium on Molten Salts, C. Hussey, D. Newman, G. Mamantov, and Y. Ito, Eds., Proceedings Volume 94-13, pgs. 483-490, The Electrochemical Society, Pennington, NJ (1994).
- 133. Robert A. Mantz, R. A. Osteryoung, Paul C. Trulove, Richard T. Carlin and Hanna Sierzputowska-Gracz, "ROESY NMR of Basic Ambient Temperature Chloroaluminate Ionic Liquids", Proceedings of Ninth International Symposium on Molten Salts, C. Hussey, D. Newman, G. Mamantov, and Y. Ito, Eds., Proceedings Volume 94-13, pgs. 336-342, The Electrochemical Society, Pennington, NJ (1994).
- 134. Richard T. Carlin and Robert A. Osteryoung, "A Silane-Imidazole Electroactive Film for Battery Cathodes", Proceedings of Ninth International Symposium on Molten Salts, C. Hussey, D. Newman, G. Mamantov, and Y. Ito, Eds., Proceedings Volume 94-13, pgs. 744-751, The Electrochemical Society, Pennington, NJ (1994).
- 135. Robert A. Mantz, Paul C. Trulove, Richard T. Carlin, and Robert A. Osteryoung, "ROESY NMR of Basic Ambient-Temperature Chloroaluminate Ionic Liquids", Inorg. Chem., **34**, 3846-3847 (1995).
- 136. J. Fuller, R. A. Osteryoung, and R. T. Carlin, "Rechargeable Lithium and Sodium Anodes in Chloroaluminate Molten Salts Containing Thionyl Chloride", J. Electrochem. Soc., **142**, 3632-3636 (1995).
- AFOSR Contract F49620-96-1-0097, 1 March, 1996 31 October, 1999.
- 137. J. Fuller, R. T. Carlin, and R. A. Osteryoung, "In-Situ Optical Microscopy Investigations of Lithium and Sodium Film Formation in Buffered Room Temperature Molten Salts", J. Electrochem. Soc. 143, L45 (1996).
- 138. Richard T. Carlin, Paul C. Trulove, Robert A. Mantz, John J. O'Dea and Robert A. Osteryoung, "Electron Transfer Kinetics for Weakly-Bonded Labile Metal-Ligand Complexes", Royal Society of Chemistry, Faraday Transactions, Special Issue on Electrochemistry Honoring Roger Parsons, **92**, 3969-3973 (1996)

- 139. Robert A. Mantz, Paul C. Trulove, Richard T. Carlin, and Robert A. Osteryoung, "Gutmann Acceptor Properties of LiCl, NaCl, and KCl Buffered Ambient-Temperature Chloroaluminate Ionic Liquids", Proceedings of Tenth International Symposium on Molten Salts, R. T. Carlin, S. Deki, M. Matsunaga, D.S. Newman, J. R. Selman and G. R. Stafford, Eds., Proceedings Volume 96-7, pgs. 104-115, The Electrochemical Society, Pennington, NJ (1996).
- 140. Dawn King and Robert A. Osteryoung "Acidity of HCl in Neutral Buffered Chloroaluminate Molten Salts", ", Proceedings of Tenth International Symposium on Molten Salts, R. T. Carlin, S. Deki, M. Matsunaga, D.S. Newman, J. R. Selman and G. R. Stafford, Eds., Proceedings Volume 96-7, pgs. 80-91, The Electrochemical Society, Pennington, NJ (1996)
- 141. Acidity of HCl in Neutral Buffered Chloroaluminate Molten Salts, Dawn King, Robert Mantz, and Robert A. Osteryoung, J. Am. Chem. Soc., **118**, 11933-11938 (1996).
- 142. Gutmann Acceptor Properties of LiCl, NaCl, and KCl Buffered Ambient Temperature Chloroaluminate Ionic Liquids, Robert A. Mantz, Paul C. Trulove, Richard T. Carlin, Terry L. Theim, and Robert A. Osteryoung, Inorg. Chem., **36**, 1227-1232 (1997)
- 143. The Room Temperature Ionic Liquid 1-Ethyl-3-Methylimidazolium Tetrafluorborate: Electrochemical Couples and Physical Properties, Joan Fuller, Richard Carlin, and Robert A. Osteryoung J. Electrochem. Soc., **144**, 3881-3886 (1997)
- 144. Anodization and Speciation of Magnesium in Chloride-Rich Room-Temperature Ionic Liquids, Joan Fuller, Richard T. Carlin, Peter Koronaios, Robert Mantz, and Robert A. Osteryoung, J. Electrochem. Soc., **145**, 24-28, (1998)
- 145. Studies on the Acidity of Neutral Buffered 1-Ethyl-3-Methylimidazolium AlCl₃ Ambient Temperature Molten Salts, Peter Koronaios, Dawn King, and Robert A. Osteryoung, Inorg. Chem. **37**, 2028-32 (1998).
- 146. Peter Koronaios and Robert A. Osteryoung, "Alkaline Earth Chlorides as Buffering Agents for Ambient Temperature Chloroaluminate Molten Salts", Proceedings of Eleventh International Symposium on Molten Salts, P.C. Trulove, H. C. De Long, G. R. Stafford, and S. Deki, Eds., Proceedings Volume 98-11, pgs. 244-251, The Electrochemical Society, Pennington, NJ (1998)
- 147. Robert Mantz, Jack Summers, and Robert A. Osteryoung, "Behavior of Oxide Containing Chloroaluminate Molten Salt, Proceedings of the Eleventh International Symposium on Molten Salts, P.C. Trulove, H. C. De Long, G. R. Stafford, and S. Deki, Eds., Proceedings Volume 98-11, pgs. 231-243, The Electrochemical Society, Pennington, NJ (1998)

- 148. CaCl₂ and MgCl₂ as Buffering Agents for Room-Temperature Chloroaluminate Ionic Liquids, Peter Koronaios and Robert A. Osteryoung, J. Electrochem. Soc., **146**, 2995-2999 (1999).
- 149. Robert A. Osteryoung, "Buffered Chloroaluminate Melts and Latent Acidity", Proceedings of the Twelfth International Symposium on Molten Salts, P.C. Trulove, H. C. De Long, G. R. Stafford, and, Eds., Proceedings Volume, The Electrochemical Society, Pennington, NJ (2000), submitted for publication.
- 150. Diffusion Coefficients of Ferrocene in Composite Materials Containing Ambient Temperature Ionic Liquids, Marek Kosmulski, Robert A. Osteryoung, and Malgorzata Ciszkowska, J. Electrochem. Soc., in press.
- 151. Use of the Ag/AgCl/Cl⁻ Electrode to Estimate Solubility Products in Ambient Temperature Ionic Liquids, Peter Koronaios and Robert A. Osteryoung, J. Electrochem Soc., submitted, December, 1999.

Appendix B:

Presentations at Meetings Related to Activities on Contract F49620-94-1-0056, 1 January, 1994 - 30 June, 1996

Invited Presentations

- 1. Robert A. Osteryoung, "Ambient Temperature Chloroalumnate Ionic Liquids: Chemistry, Electrochemistry and Witchcraft". Colloquium, Department of Chemistry, North Carolina State University, Raleigh, NC, October 7, 1996..
- 2. Robert A. Osteryoung, "Ambient Temperature Chloroaluminate Ionic Liquids: Chemistry, Electrochemistry and Witchcraft". Colloquium, Department of Chemistry, Colorado State University, Ft. Collins, CO, May 29, 1997.
- 3. Robert A. Osteryoung, "'Ambient Temperature Chloroalumnate Ionic Liquids: Chemistry, Electrochemistry and Witchcraft". Eltron Research, Inc., Boulder, CO, May 30, 1997.
- 4. Robert A. Osteryoung, "Some Studies of Latent and Bronsted Acidity in Ambient Temperature Chloroaluminate Molten Salts", Gordon Research Conference on Molten Salts and Metals, Henniker, NH, August, 1997.
- 5. Robert A. Osteryoung, "Acidity of and In Ambient Temperature Chloroaluminate Ionic Liquids", Frontiers in Electrochemistry Symposium Honoring Stanley Bruckenstein, American Chemical Society Fall Meeting, Las Vegas, Sept. 6-13, 1997.
- 6. Robert A. Osteryoung, "Ambient Temperature Chloroaluminate Ionic Liquids: Chemistry, Electrochemistry, and Witchcraft", Department of Chemistry Colloquium, Louisiana State University, Baton Rouge, LA, October 31, 1997.
- 7. Robert A. Osteryoung, "Ambient Temperature Chloroaluminate Ionic Liquids: Chemistry, Electrochemistry, and Witchcraft", Department of Chemistry Colloquium, Brooklyn College, CUNY, March 11, 1998.
- 8. Peter Koronaios and Robert A. Osteryoung, "Alkaline Earth Chlorides as Buffering Agents for Ambient Temperature Chloroaluminate Molten Salts", Eleventh International Symposium on Molten Salts, The Electrochemical Society, Spring Meeting, San Diego, May, 1998.
- 9. Robert Mantz, Jack Summers, and Robert A. Osteryoung, "Behavior of Oxide Containing Chloroaluminate Molten Salts", Eleventh International Symposium on Molten Salts, The Electrochemical Society, Spring Meeting, San Diego, May, 1998.

- 10. Robert A. Osteryoung, "Superacidity in Ambient Temperature Chloroaluminate Ionic Liquids", Symposium on Electrochemistry in Unusual Media and Under Unusual Conditions, The Electrochemical Society, Spring Meeting, San Diego, May, 1998.
- 11. Robert A. Osteryoung, "Coordination Chemistry, Acid-base Chemistry and Electrochemistry in Ambient Temperature Ionic Liquids", California Institute of Technology, Inorganic Division Seminar, July 29, 1998.
- 12. Robert A. Osteryoung, "Acidity in Ambient Temperature Chloroaluminate Ionic Liquids", Symposium on Thermodynamic Predictions and Applications", The Metallurgical Minerals and Materials Society of AIME, San Diego, CA, Feb. 28 March 4, 1999.
- 13. Robert A. Osteryoung, "Ambient Temerature Chloroaluminate Ionic Liquids An Overview", International Chemical Conference, Taipei, Taipei, Taiwan, May 13, 1999.
- 14. Robert A. Osteryoung, "Ambient Temerature Chloroaluminate Ionic Liquids An Overview", Chemistry Department, National Sun Yat-Sen University, Kaohsiung, Taiwan, May 18, 1999.
- 15. Robert A. Osteryoung, "Ambient Temerature Chloroaluminate Ionic Liquids An Overview", Chemistry Department, University of Hong Kong, May 20, 1999.
- 16. Robert A. Osteryoung, "Buffered Chloroaluminate Melts and Latent Acidity", Twelfth International Symposium on Molten Salts, The Electrochemical Society, Fall Meeting, Honolulu, HI, October, 1999.
- 17. Paul C. Trulove, Robert A. Mantz, High C. DeLong, and Robert A. Osteryoung, "Studies of Cation Transport in Molten Salts and Molten Salt-Polymer Gels by Pulsed-Field-Gradient Spin-Echo NMR", Twelfth International Symposium on Molten Salts, The Electrochemical Society, Fall Meeting, Honolulu, HI, October, 1999.

Contributed Presentations

- 1. Boris Ravdel and Robert A. Osteryoung, The Potentiometric and Galvanostatic Behavior of Polypyrrose Films in ambient Temperature Chloroaluminate Molten Salts", North Carolina ACS Section Meeting, Durham, NC, April, 1997.
- 2. Peter Koronaois and Robert A. Osteryoung, Studies of the Acid-Base Properties of Neutral Buffered Room-Temperature Chloroaluminate Ionic Liquids, North Carolina ACS Section Meeting, Durham, NC, April, 1997.
- 3. Shawn R. Campagna, Peter Koronaios, Robert A. Osteryoung, and Charles R. Cornman, Spectroscopy and Coordination chemistry in Room-Temperature Ionic Liquids, (Poster), American Chemical Society, Spring Meeting, Anaheim, CA March 21-25, 1999.

4. Peter Koronaios, Robert A. Osteryoung, Acidity of Neutral Buffered 1-ethyl-3-methylimidazoliumChlorideAluminium Chloride Ionic Liquids, North Carolina ACS Section Meeting, Chapel Hill, NC, April 24, 1999